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ORIGINAL PAPER

An Analysis of Shear-Dependent Mechanochemical Reaction Kinetics

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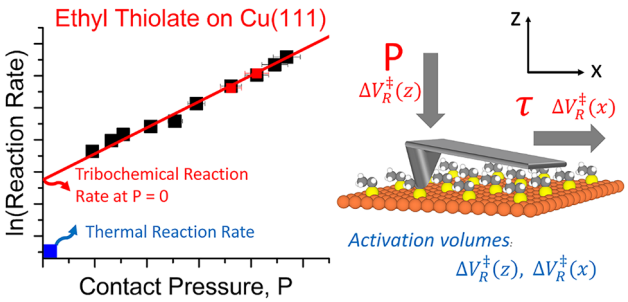
Abstract

This paper shows how the effect of combined normal and shear stresses on the rates of tribochemical reactions can be calculated using Evans-Polanyi (E-P) perturbation theory. The E-P approach is based on transition-state theory, where the rate of reaction is taken to be proportional to the concentration of activated complex. The equilibrium constant depends on the molar Gibbs free energy change between the initial- and transition-states, which, in turn, depends on the stresses. E-P theory has been used previously to successfully calculate the effects of normal stresses on reaction rates. In this case, ln(Rate) varies linearly with stress with a slope given by an activation volume, which broadly corresponds to the volume difference between the reactant and activated complex. An advantage of E-P theory is that it can calculate the influence of several perturbations, for example, the normal stress dependence of the shear stress during sliding. In this paper, E-P theory is used to calculate shear-induced, tribochemical reaction rates. The results depend on four elementary activation volumes for different contributions to the Gibbs free energy: two of them due to normal and shear stresses for sliding over the surface and two more for the surface reaction. The results of the calculations show that there is a linear dependence of ln(Rate) on the normal stress but that the coefficient of proportionality between the ln(Rate) and the normal stress now has contributions from all elementary-step activation volumes. Counterintuitively, the analysis predicts that the ln(Rate)-normal stress evolution tends, at zero normal stress, to an asymptotic rate constant that depends on sliding velocity and differs from the thermal reaction rate. The theoretical prediction is verified for the shear-induced decomposition of ethyl thiolate species adsorbed on a Cu(100) single crystal substrate that decomposes by C−S bond cleavage. The theoretical analyses show that tribochemical reactions can be influenced by either just normal stresses or by a combination of normal and shear stresses, but that the latter effect is much greater. Finally, it is predicted that there should be a linear relationship between the activation energy and the logarithm of the pre-exponential factor of the asymptotic rate constant.

Graphical Abstract



Keywords Evans · Polanyi perturbation theory · Shear · Stress · Induced processes · Thermodynamic analysis · Tribochemistry

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1 Introduction

Because of the difficulty of analyzing solid solid-interfaces, it has been challenging to identify the mechanisms of tribochemical reactions and to understand the differences between thermal and tribochemical reaction rates. Various effects such as electron emission at the sliding interface [2] or local temperatures that were supposed to be higher than those predicted by theory [3] have been proposed to account for the differences. Tribochemical reactions occurring under so-called extreme-pressure conditions could be analyzed by assuming that the local flash temperatures evolved in to a relatively high (up to 1000 K) thermodynamic temperature [4] that could be used to effectively model the lubrication behavior [5, 6]. This model was not able to describe the behavior occurring under milder conditions. However, it eventually became clear that tribochemical reactions occurring at lower temperatures, as well as other processes such as friction and viscosity had identical conceptual and theoretical underpinnings [7]: that the applied stresses coupled directly into the process to modify (and ideally lower) the energy barrier to change the reaction rate. This general concept was first proposed by Prandtl for sliding friction [8] and by Eyring for viscosity [9]. This prompted a search for an analogous method that could be applied to analyzing stress-modified chemical reactions. A suitable approach was proposed by Evans and Polanyi [10, 11] in the 1930's based on the concepts of transition-state theory [12]. Note that this is different from the linear-free-energy relations, also named for Evans and Polanyi, that have been used to model catalytic reaction kinetics [13–15].

As conventionally analyzed, transition-state theory assumes that the reactant and the transition-state (activated complex) structures are in thermodynamic equilibrium and uses statistical thermodynamics to calculate an equilibrium constant between them to obtain a reaction rate constant [12]. Instead, Evans and Polanyi used a classical thermodynamic analysis to calculate the effect of perturbations such as hydrostatic pressure P on the rate constant [16, 17]. The theory is outlined in greater detail below.

Conceptually, one can distinguish between processes such as chemical reactions occurring due to just normal stresses, which are broadly characterized as mechanochemistry and those occurring due to combined normal and shear stresses such as tribochemistry, friction or viscous flow that can be characterized as tribological processes.

We have previously studied the normal-stress-modified reaction of methyl thiolate species adsorbed on Cu(100) using Evans-Polanyi perturbation theory [10, 11]. A 'theoretical' experiment is carried out by compressing the surface structures of the initial- and transition-states to calculate the energy a function of the distance from the surface using quantum mechanics to obtain a change in free energy as a function of the normal stress. This, in turn, can be used to calculate how the reaction rate constant changes and yielded good agreement with the experimental results [18]. We have recently extended this approach to studying the influence of hydrostatic pressure on reactions occurring in a fluid using the extreme-pressure polarizable continuum (XP-PCM) model [19–22] applied to Diels–Alder coupling reactions.

As noted above, tribochemical reactions occur while sliding under the influence of a normal stress. Sliding shear can induce the decomposition of alkyl thiolates adsorbed on Cu(100) [23] or carboxylates on copper [24–26] and can induce pathways that are not thermally accessible [27]. It has also been found that the rate of mechanochemical decomposition of longer-chain carboxylates, where the terminal group can be changed to alter the tip surface interaction, does not appear to influence the reaction rate [26]. This conclusion is counterintuitive and disagrees with predictions from molecular dynamics simulation [28].

The following analyzes the kinetics of combined normal- and shear-stress-induced tribochemical reactions of adsorbates on surfaces using Evans and Polanyi perturbation theory [10, 11]. An advantage of this approach is that it can simultaneously include the effects of multiple perturbations. This capability has been used to analyze the normal-stress dependence of sliding shear stresses [1] to yield results that are in agreement with an experimental equation for the velocity- and temperature-dependences of the friction of Langmuir–Blodgett films proposed by Briscoe and Evans [29]. In the following, we outline an extension of this approach to describe the effect of combined normal and shear stresses on the rates of chemical reactions.

2 Application of Evans-Polanyi Perturbation Theory to Stress-Modified Processes

The general approach for analyzing the effect of stresses exerted on a surface adsorbate using the Evans-Polanyi perturbation theory is illustrated by Fig. 1. Figure 1(a) shows a generic energy profile showing the form of the potential energies around the initial and transition states within an $x-z$ plane coincident with the reaction profile. The application of E-P theory to sliding friction using this model is described in detail in reference [1] and the theoretical outline given below is an extension of this analytical approach. The energetics described in Fig. 1(a) could either be due to the transition from one site to the next to model sliding friction, or a chemical reaction, such as methyl thiolate decomposition. The analysis described below specifically

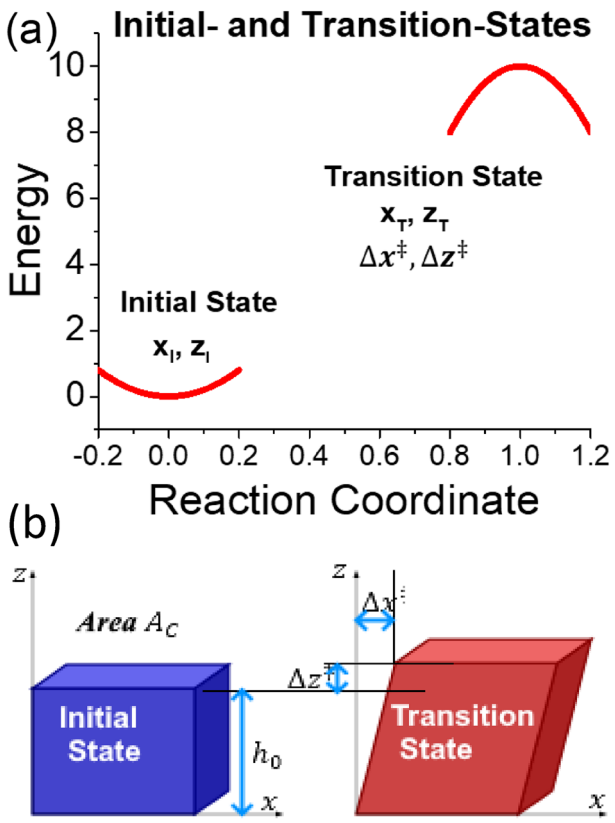

Fig. 1 **a** Plot of the potential energy profile for analyzing a pressure-dependent shear strength from an initial state to a transition state, **b** an illustration of the deformations from the initial-state structure to the transition state used in the analytical model. Published with permission from Springer Nature from Ref. [1]

applies to sliding on surfaces but this encompasses a range of mechanical systems that will facilitate the development of more general theories.

The parameters that control shear-induced reactions are the normal force, the reaction temperature, T and the sliding velocity, v. As in the calculation of the pressure-dependent shear stresses [1], the stress-dependent term of the Gibbs free energy equals the reversible work carried out between the final state and an arbitrary reference configuration [30]. Note that this depends on the magnitude and the direction of the applied force relative to the reactant. In the following analysis, we make the approximation that the initial- and transition state structures are rigid and do not deform under the influence of the applied force. This is equivalent to a Bell-model analysis [31]. Thus, the molar Gibbs free energy, G_I^0, of an initial-state structure is given by:

$$G_I^{0R} = U_I^{0R} - TS_I^{0R} + \sigma_z\left(V_{I,z}^{0\ R} - V_{Ref,z}^{0\ R}\right) + \tau_{xz}^I\left(V_{I,x}^{0\ R} - V_{Ref,x}^{0\ R}\right) \tag{1}$$

where τ_{xz}^I is the shear stress along the x direction with a normal stress σ along z (see Fig. 1) acting on the initial-state structure [30]. The superscripts, R, refer to species involved in the chemical reaction to differentiate from parameters due to sliding and $V_{I,z}^{0\ R}$ and $V_{I,x}^{0\ R}$ are the initial-state volumes associated with sliding along the z and x directions measured relative to some arbitrary references volumes $V_{Ref,z}^{0\ R}$ and $V_{Ref,x}^{0\ R}$. Note that the magnitude of the shear stress τ_{xz}^I for a particular normal stress depends on the nature of the adsorbate [1] and the individual stresses and the volumes constitute conjugate pairs [30] analogous to the PV term for hydrostatic pressure.

An analogous equation for the transition-state structure is:

$$G_T^{0R} = U_T^{0R} - TS_T^{0R} + \sigma_z\left(V_{T,z}^{0\ R} - V_{Ref,z}^{0\ R}\right) + \tau_{xz}^T\left(V_{T,x}^{0\ R} - V_{Ref,x}^{0\ R}\right), \tag{2}$$

where τ_{xz}^I and τ_{xz}^T differ because they depend on the friction coefficients of different adsorbed overlayers, the reactant structure and the transition-state structure. The difference between the Gibbs free energies of the initial- and transition-state structures is obtained by combining Eqns. 1 and 2 and yields:

$$\begin{aligned}\Delta G^{0R} = {} & \Delta U^{0R} - T\Delta S^{0R} + \sigma_z\left(V_{T,z}^{0\ R} - V_{I,z}^{0\ R}\right) \\ & + \tau_{xz}^T\left(V_{T,x}^{0\ R} - V_{Ref,x}^{0\ R}\right) - \tau_{xz}^I\left(V_{I,x}^{0\ R} - V_{Ref,x}^{0\ R}\right)\end{aligned} \tag{3}$$

However, the change in Gibbs free energy must be independent of the choice of reference configuration, which can only be the case when $\tau_{xz}^T = \tau_{xz}^I = \tau_{xz}(P, T.v)$. This is because the stresses are averaged over all adsorbates in the contact, but the relative coverages of reactants and products vary as the reaction proceeds. This causes the shear stress, and therefore the friction coefficient to vary during the reaction. The resulting shear stress is therefore not constant but depends on the extent of the reaction. This effect has been used to measure mechanochemical reaction rates [32]. That is, $\tau_{xz}(P, T, v)$ depends on the state of the system. To remove the reference-state dependence in Eq. 3, it is assumed that the change in friction force is relatively modest so that τ_{xz} can be considered to be approximately constant so that Eq. 3 becomes:

$$\begin{aligned}\Delta G^{0R} = {} & \Delta U^{0R} - T\Delta S^{0R} + \sigma_z\left(V_{T,z}^{0\ R} - V_{I,z}^{0\ R}\right) \\ & + \tau_{xz}^T\left(V_{T,x}^{0\ R} - V_{I,x}^{0\ R}\right) = \Delta U^{0R} - T\Delta S^{0R} + \sigma_z\Delta V_z^{0R} + \tau_{xz}^T\Delta V_x^{0R},\end{aligned} \tag{4}$$

where $\Delta V_z^{0R} = \left(V_{T,z}^{0\ R} - V_{I,z}^{0\ R}\right)$ and $\Delta V_x^{0R} = \left(V_{T,x}^{0\ R} - V_{I,x}^{0\ R}\right)$ are the molar activation volumes for the reaction within a Bell approximation. They depend on the activation length (Fig. 1) as $\Delta V_x^{0R} = \Delta x^{\ddagger}A_C$ and $\Delta V_z^{0R} = \Delta x^{\ddagger}A_C$, where A_C is the area over which the stress acts [1, 33] and is known as

the Stearn-Eyring approximation. Using Evans-Polanyi theory, and putting $\sigma_z = -P$ and $\tau_{xz} = -\tau$, the effective reaction rate constant under the influence of combined normal and shear stresses, k^R_{Sld}, is:

$$\ln k^R_{Sld} = ln k^R_0 + \frac{P\Delta V^{0R}_z}{RT} + \frac{\tau \Delta V^{0R}_x}{RT} \tag{5}$$

where k^R_0 is the thermal reaction rate constant that depends on ΔU^{0R} and $T\Delta S^{0R}$. Note that negative values of the activation volumes lead to an increase in the reaction rate. It is now necessary to use a pressure-dependent shear stress, $\tau = -\left(\frac{\Delta V^{0S}_z}{\Delta V^{0S}_x}\right)P + \frac{RT}{\Delta V^{0S}_x} ln\left(\frac{v}{v_0}\right)$, which was derived in Ref. 1 using Evans-Polanyi theory and uses the same convention as above that $\sigma_z = -P$ and $\tau_{xz} = -\tau$ [1]. In this case, ΔV^{0S}_z and ΔV^{0S}_x are the elementary-process molar activation volumes associated with interfacial sliding and $v_0 = k^S_0 \Delta x^{\ddagger}$, where k^S_0 is the rate constant for the tip to transit from one site to the next. The activation energy for this process will be much lower than that for the reaction and energy barriers that are comparable with RT will have to include the influence of both forward and reverse motions as in Eyring viscosity theory [9, 34]. Here, the normal stress implicitly includes adhesion effects. This leads to a general formula for a pressure-dependent reaction rate given by:

$$\begin{aligned} \ln k^R_{Sld}(P,v,T) = &\left(ln k^R_0 + \frac{\Delta V^{0R}_x}{\Delta V^{0S}_x} ln\left(\frac{v}{v_0}\right)\right) \\ &+ \frac{P}{RT}\left(\Delta V^{0R}_z - \Delta V^{0R}_x \frac{\Delta V^{0S}_z}{\Delta V^{0S}_x}\right) \end{aligned} \tag{6}$$

In this case, the effective shear activation volume is a composite of the elementary-process activation volumes for friction and reactions; $\Delta V^{0\ R}_{Sld} = \Delta V^{0R}_z - \Delta V^{0R}_x \frac{\Delta V^{0S}_z}{\Delta V^{0S}_x}$. Note that this equation is similar to that proposed by Ward for polymer fracture [35], presumably because that also occurs via activated processes. Note that the normal-stress-induced component, ΔV^{0R}_z, can be measured independently just by compressing the adsorbate [18, 36]. However, the intercept at zero pressure of a plot of ln(*Rate*) versus normal stress does not equal $ln k^R_0$, the natural logarithm of the thermal rate constant, as might be expected intuitively. This result implies that the shear-dependent change in reaction rate is not due only to a change in the activation volume, but also to a change in the rate extrapolated to zero stress. Tables of activation volumes for shear-induced reactions do not account for all the effects that influence their rates [37], while the corresponding values for normal-stress-induced reactions do [16, 17]. This effect will be illustrated for the mechanically induced decomposition of ethyl thiolate species on a Cu(100) substrate, for which the thermal rate has been measured [38]. Note that the reaction rates of methyl and ethyl thiolate have also been investigated but show critical effects below which there is no mechanochemical reactivity [23], thus potentially influencing the value of the intercept at zero stress.

3 Compensation Effects in Stress-Modified Processes

A correlation has been found experimentally between the activation energies and pre-exponential factors for some chemically similar catalytic reactions such that a change in the reaction activation energy varies linearly with a change in lnA, where A is the pre-exponential factor. This is known as a compensation effect, although its origin in catalysis is not well understood [39–41] but it has been observed in molecular-dynamics simulations of adsorbed phosphate esters [42]. As shown below, this arises naturally from the above analysis.

As indicated above, the formulae for the intercept in Eq. 6, $\ln k^R_{Sld}(0) = \left(ln k^R_0 + \frac{\Delta V^{0R}_x}{\Delta V^{0S}_x} ln\left(\frac{v}{v_0}\right)\right)$, depends on $\frac{\Delta V^{0R}_x}{\Delta V^{0S}_x}$, written as α_S, a coupling parameter, to give $\ln k^R_{Sld}(0) = \left(ln k^R_0 + \alpha_S ln\left(\frac{v}{v_0}\right)\right)$. This can be written as $k^R_{Sld}(0) = k^R_0 \left(\frac{v}{k^S_0 \Delta x^{\ddagger}}\right)^{\alpha_S}$ and the rate constants can be expressed in their Arrhenius forms as: $k^R_0 = A^R_0 exp\left(-E^R_0/RT\right)$, $k^R_{Sld}(0) = A^R_{Sld}(0) exp\left(-E^R_{Sld}(0)/RT\right)$ and $k^S_0 = A^S_0 exp\left(-E^S_0/RT\right)$, where E^R_0, $E^R_{Sld}(0)$ and E^S_0 are the corresponding activation energies. Substituting for the Arrhenius forms of the rate constants in the above equation gives:

$$\begin{aligned} A^R_{Sld}(0) exp\left(-\frac{E^R_{Sld}(0)}{RT}\right) = &\ v^{\alpha_S} A^R_0 exp\left(-E^R_0/RT\right) \\ &/\left(\left(\Delta x^{\ddagger}\right)^{\alpha_S} \left(A^S_0\right)^{\alpha_S} exp\left(-\alpha_S E^S_0/RT\right)\right) \end{aligned} \tag{7}$$

Collecting terms gives: $E^R_{Sld}(0) = E^R_0 - \alpha_S E^S_0$ and $A^R_{Sld}(0) = A^R_0 \left(\frac{v}{\Delta x^{\ddagger} A^S_0}\right)^{\alpha_S}$. Each equation depends on the common variable, α_S, which can be eliminated to yield:

$$E^R_{Sld}(0) = \left(E^R_0 - \frac{E^S_0 \ln\left(A^R_0\right)}{\ln\left(v/v_C\right)}\right) - \frac{E^S_0}{\ln\left(v/v_C\right)} \ln A^R_{Sld}(0) \tag{8}$$

where $v_C = \Delta x^{\ddagger} A^S_0$, is a characteristic velocity and predicts a linear relationship between the asymptotic values of the activation energy, $E^R_{Sld}(0)$, and the natural logarithm of the pre-exponential factors, $lnA^R_{Sld}(0)$. It is noted that this equation arises naturally from an Evans-Polanyi analysis

of shear-induced mechanochemical reactions and, strictly speaking, applies only to adsorbates. A linear compensation effect plot implies that the values of k_0^R and k_0^S are relatively independent of the nature of the functional groups attached to the mechanophore.

4 Experimental Methods

Experiments were carried out using an RHK Variable Temperature Ultrahigh Vacuum (UHV) 750 atomic force microscope (AFM) operating at a base pressure of ~ 2×10^{-10} Torr following bakeout. The apparatus also contained an analysis chamber for sample cleaning and was equipped with a SPECTALEED Scienta Omicron combined low-energy electron diffraction (LEED)/Auger system for assessing sample cleanliness. The chamber was also equipped with a Dycor quadrupole mass spectrometer for leak checking and background gas analysis. The Cu(100) single crystal was cleaned by argon ion bombardment (~ 1 kV, ~ 2 μA/cm^2) and then by annealing to ~ 850 K to remove any surface damage induced by the cleaning procedure. A saturated overlayer of ethyl thiolate species was prepared by dosing a clean Cu(100) sample held at ~ 298 K in UHV by background dosing at a pressure of 1×10^{-8} Torr of diethyl disulfide (DEDS, Aldrich, 99.0% purity) or ethanethiol (ET, Aldrich, 99.0% purity) for 200 s, where the pressures were measured using a nude ionization gauge included in the UHV chamber, and were not corrected for ionization gauge sensitivity [43]. The DEDS or ET were transferred to glass bottles and attached to the gas-handling system of the vacuum chamber and cleaned by several freeze-pump-the cycles. The purities were monitored using mass spectrometry.

Sliding-stress-induced mechanochemical reactions were carried out by applying normal forces using a silicon μ-masch (HQ:NSC19/NO AL) AFM tip with a nominal 8 nm radius and sliding at a speed of 120 nm/s. The reaction rate was measured for reciprocal sliding at various loads from the variation in the depth of the groove as a function of the number of passes. The width of the groove was used to estimate the contact area of the AFM tip with the surface [23]. The cantilever force constant was obtained from the geometry of the cantilever measured by scanning electron microscopy, as described in reference [44] and by the Sader method [45]. SEM was also used to measure the radius of the AFM tip after performing the experiments. The measured cantilever tilt angle in the RHK AFM is ~ 22.5°, so that a tilt correction was applied as suggested by Hutter [46] using the values of the length of the cantilever and the length of the tip, obtained from a scanning electron microscope image of the cantilever. These values were used to calculate the normal stress at the center of the contact. Force-distance curves measured between experiments verified that tips remained stable over multiple sliding experiments. The protocols used for analyzing the mechanochemical reaction kinetics are outlined in detail in the Supplementary Information section.

5 Results

The reaction rates were measured at room temperature (298 K) using reciprocal sliding for various numbers of scans and the loss of ethyl thiolate species was measured from the depth of the wear track by collecting AFM images at non-perturbative loads. Typical results are displayed in Fig. 2, which show the development of lines in the position that the tip had rubbed at higher loads. Experiments were carried out with both ethane thiol (ET) and diethyl disulfide (DEDS), which should produce identical surface species [32, 38]. This is corroborated by measuring identical pull-off forces for saturated overlayers formed from ET and DEDS (see Figure S2). Plots of the depth of the

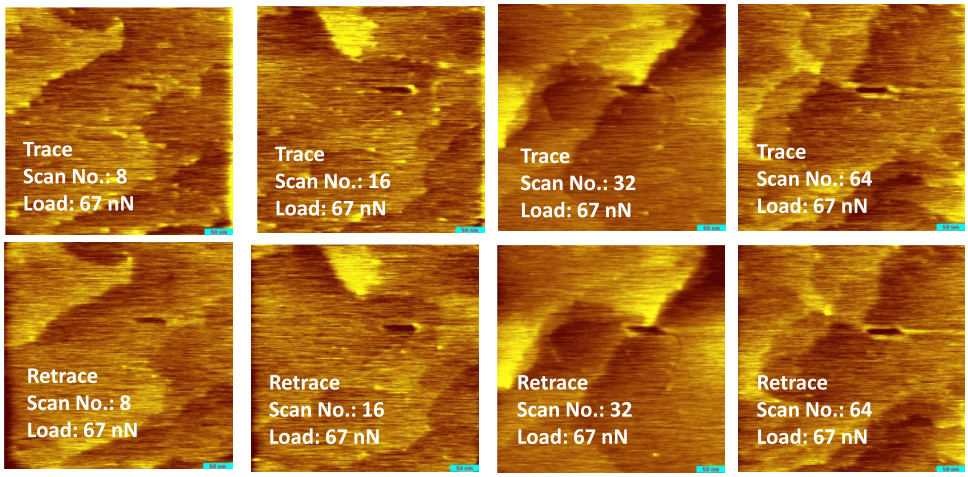

Fig. 2 Low-load AFM images of ethyl-thiolate-covered Cu(100) after having been scanned various times at a load of 67 nN

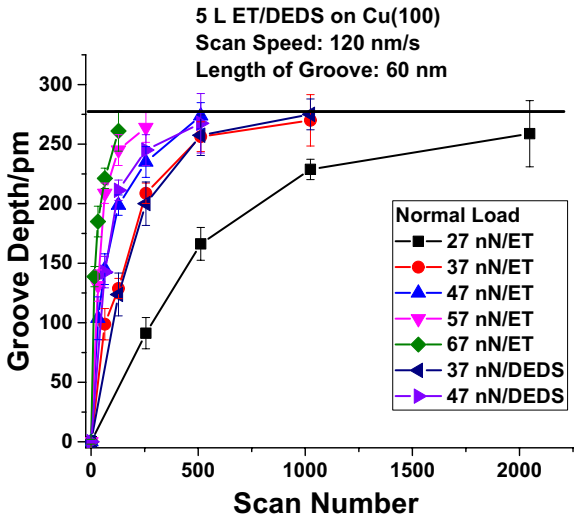

Fig. 3 Plot of the depth of the wear track of an ethyl-thiolate-covered Cu(100) surface formed from either DEDS or ET and a function of the number of scans with various plied loads. The data show and exponential increase in groove depth up to a maximum of ~ 270 pm, which agrees well with an estimated height of an adsorbed ethyl thiolate species on the surface

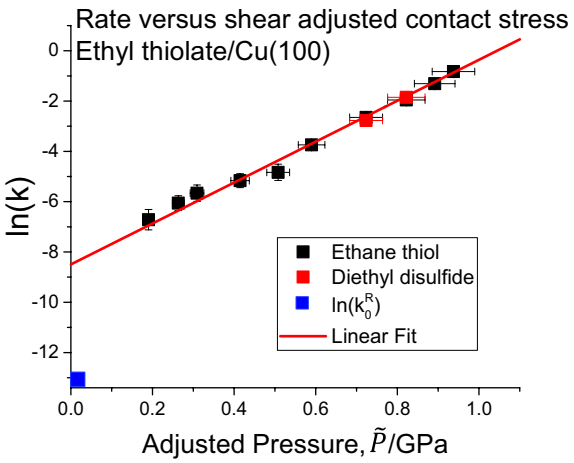

Fig. 4 Plot of ln(k), where k is the rate of ethyl thiolate decomposition on a Cu(100) surface, as a function of adjusted normal stress, $\widetilde{P}$, in gigaPascals (GPa). The ethyl thiolate was formed from either DEDS (■) or ET (■). Also shown is the value of ln(k) for the thermal reaction obtained from temperature-programmed desorption experiments (■) shown at zero stress to emphasize that it differs from the intercept of the linear fit (shown as a solid red line) extrapolated to zero normal stress

grooves as a function of the number of scans using various normal loads are shown in Fig. 3.

Exponential fits to the data are shown that indicate that the tribochemical reaction proceeds via a first-order process as found previously for methyl thiolate decomposition measured using a ball-on-flat geometry in UHV [47, 48]. These data were collected for various normal loads and the reaction rate constants measured as a function of the normal stress at a sample temperature of 290 K and a sliding speed of 120 nm/s. The depth increases exponentially up to a saturation value of ~ 280 pm, indicated by a horizontal line on the figure. This depth agrees well with an estimated length of an adsorbed ethyl thiolate species. The data were analyzed by calculating the normal stresses from the applied normal loads and the contact areas measured either from the width of the indent for a tip compressing the surface or from the width of the groove for a tip sliding over the surface [18]. The reaction rate constants for each stress are obtained from an exponential fit to the data and the results are plotted as ln(*Rate*) versus an adjusted pressure, $\widetilde{P}$, in gigaPascals (GPa), where the methods for calculating the adjusted normal pressure is described in detail in the Supplementary Information section where adjusted pressure was corrected to take into account the pressure distribution across the contact. This results in the plot shown in Fig. 4, which yields an asymptotic value of $\ln k_{Sld}^{R}(0) = -8.49 \pm 0.15$ and a sliding activation volume, $\Delta V_{Sld}^{0\ R} = -33.5 \pm 0.7$ Å^3/molecule (-55.6 ± 1.2 cm^3/mol) from the slope. The data for films formed from ET and DEDS are essentially identical confirming that they both react to form adsorbed ethyl thiolate species on the surface. A linear fit reproduced the data very well (with an R^2 value of 0.996).

6 Discussion

A major prediction from the theory described above is that the change in reaction rate under the influence of a combined normal and shear stresses depends both on a change in the activation volume and a change in the intrinsic rate. Note that the shear- and pressure-dependencies of the rates depend on several elementary-step activation volumes thereby complicating the analysis of shear-induced results compared to those being induced just by normal stresses, even in cases where the normal and shear dependences have been measured independently [49].

The shear-induced decomposition of ethyl thiolate species has been studied on a Cu(100) surface and the desorption products measured using temperature-programmed desorption (TPD) [38], where the adsorbed thiolate desorbs with a peak temperature of 406 K when using a heating rate of 4.2 K/s to yield a value of $lnk_0^R = -13.28$ when using a standard pre-exponential factor of 1×10^{13} s^{-1} [50]. This value is plotted as a blue square in Fig. 4 and is clearly well below the asymptote. A similar analysis of TPD data was used to yield a rate constant for the normal-stress-induced decomposition of methyl thiolate on copper that was in good

agreement with both the prediction from quantum theory [51] and with the rate found when extrapolating ln(*Rate*) versus *NormalStress* to zero stress for a compressed system [18]. Here, the intercept is predicted to equal lnk_0^R. In contrast, for a shear-induced reaction, extrapolation of a plot of ln(*Rate*) versus *NormalStress* to zero stress does not yield an intercept that corresponds to the thermal reaction rate and gives $\ln k_{Sld}^R(0) = -8.49 \pm 0.15$. Note that the asymptote would still be much larger than the thermal rate even if the average stress had been used or if a slightly different pre-exponential factor had been used to obtain the rate. Thus, the results in Fig. 4 confirm the general theoretical conclusion that a change in a shear-induced tribochemical reaction rate originates from both a change in the intrinsic rate and change in the activation volume. The difference between the two rates, $\ln k_{Sld}^R(0) - lnk_0^R = 4.8 \pm 0.2$. This contributes to approximately two orders of magnitude increase in the reaction rate, independent of any effects due to a change in activation volume. In part, this accounts for the much lower normal stresses required to induce a reaction by shear than under normal stresses alone. It should be emphasized that the reaction is accelerated by just a normal stress, just to a lesser extent. The velocity-dependence of the intercept may also account for the lack of sensitivity to the strength of the tip-surface interaction for experiments carried out at low sliding speeds [26] compared to the results of molecular-dynamics simulation where the sliding speed is much higher [28].

From the above analysis, the difference in the logarithms of the rate constants equals $\frac{\Delta V_R^{\ddagger}(x)}{\Delta V_S^{\ddagger}(x)} ln\left(\frac{v}{v_0}\right) = \alpha_S ln\left(\frac{v}{v_0}\right) = 4.8 \pm 0.2$. Typically the plateau of lateral force versus sliding speed plots of self-assembled monolayers measured using an atomic-force microscope (AFM) occurs at a sliding speed of ~ 5000 nm/s [52]. A simple model for the velocity dependence of the sliding force in an AFM [53, 54] shows that that occurs when $ln\left(\frac{v}{v_0}\right) \approx 2$, suggesting that, for these tribochemical reaction experiments, $v_0 \approx 680$ nm/s. The sliding speed used to measure the ethyl thiolate decomposition rate was 120 nm/s and, assuming a similar value of v_0 for the thiolate overlayer, yields a value of $\alpha_S = -2.8 \pm 0.2$. This allows us to estimate a value for $\Delta V_R^{\ddagger}(Sld) = \Delta V_R^{\ddagger}(z) - \alpha_S \Delta V_S^{\ddagger}(z)$. The activation volume for the normal-stress-induced reaction, $\Delta V_R^{\ddagger}(z)$, has not been measured for ethyl thiolate on Cu(100) but has been measured for adsorbed methyl thiolate and is ~ − 20 Å^3/molecule [18]. Since $\Delta V_S^{\ddagger}(z) = \frac{1}{\alpha_S}\left(\Delta V_R^{\ddagger}(z) - \Delta V_R^{\ddagger}(Sld)\right)$, assuming that $\Delta V_R^{\ddagger}(z)$ is similar for ethyl thiolate leads to a value of $\Delta V_S^{\ddagger}(z) \sim -0.18$ Å, which is due to the topological corrugation of the surface potential (see Fig. 1). We note that this is an upper limit because the value of $\Delta V_R^{\ddagger}(z)$ is likely to be larger for an ethyl thiolate overlayer than for methyl thiolate that would result in a lower value of the surface corrugation.

7 Conclusions

A model has been developed for shear-induced tribochemical reactions for a simple adsorbate anchored to a rigid substrate. The change in reaction rate depends on a modification of the activation volume that includes contributions from both the normal stress and sliding, as well as a baseline change in the reaction rate. The latter effect is evidenced by an asymptotic value of the rate constant at zero stress that is different from the intrinsic, thermal reaction rate. In the case of the decomposition of ethyl thiolate species on Cu(100), this contributes to an approximately two-orders-of-magnitude increase in the rate. This is a key feature of the proposed model and the observed difference in the rates as the stresses approach zero compared to the thermal rate for ethyl thiolate decomposition provides evidence that the model is reasonable.

The intercept and the slope of the logarithm of the rate versus contact stress depend on a coupling parameter,$\alpha_S = \frac{\Delta V_x^{0R}}{\Delta V_x^{0S}}$, where ΔV_x^{0R} is the activation volume for the reaction along the shear direction and ΔV_x^{0S} is the corresponding value for sliding friction. Eliminating this parameter from the formula for the intercept of the plot of ln(*Rate*) versus *ContactStress* leads to a relationship between the activation energy and the pre-exponential factor of the asymptotic rate that is reminiscent of the compensation effects that have been observed in catalytic reactions.

The theoretical analysis presented here will provide a basis for analyzing and interpreting the results of shear-induced mechanochemical reactions to help in identifying the meaning of the experimental parameters. In particular, the activation volume, which fully describes the effect of an applied stress on reactions induced by a static stress, does not provide a full description of shear -induced reactions. The concepts used in the present analysis will guide the development of predictive models where the theory and experiment can be stringently compared and will enable lubricant additives to be designed based on a knowledge of how specific parameters influence the tribochemical reactivity.

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Data Availability The experimental data can be found in the ESI† and manuscript and is referred to throughout the manuscript.

Declarations

Competing interests The authors declare no competing interests.

Conflicts of interest The authors declare no competing financial interest.

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